# The Electroreduction of some *N*-Haloamides[1]

Denis Bérubé, Jean Caza, Frank M. Kimmerle, and Jean Lessard
*Département de chimie, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1*

Received January 9, 1975

Denis Bérubé, Jean Caza, Frank M. Kimmerle, and Jean Lessard. Can. J. Chem. **53**, 3060 (1975).

The electroreduction of nine *N*-haloamides (ZCONRX) at a dropping mercury electrode has been investigated in protic and aprotic media. Preparative electrolysis indicated the possibility of capturing the intermediate amide radical by intermolecular addition to olefins or by intramolecular hydrogen abstraction.

Denis Bérubé, Jean Caza, Frank M. Kimmerle et Jean Lessard. Can. J. Chem. **53**, 3060 (1975).

On a étudié la réduction électrochimique de neuf *N*-haloamides (ZCONRX) à l'électrode à goutte de mercure tombante en milieu protique et aprotique. Les électrolyses préparatives laissent croire que le radical amide intermédiaire peut être capté par addition intermoléculaire à des oléfines et par abstraction intramoléculaire d'hydrogène.

Our interest in *N*-haloamides and amide radicals (1–4), and in particular in the chromous chloride promoted addition of *N*-haloamides to olefins (1, 2), led us to study the electrochemical reduction of some *N*-haloamides. It is obvious that if by an electrochemical route the reduction of the nitrogen–halogen bond leads to an amide radical $Z{-}CO{-}\dot{N}{-}R$ then a facile means of the production of a promising synthetic intermediate has been attained. Furthermore, it was hoped that the study of the electron transfer at a solid electrode would give additional insight regarding the mechanism of the transition metal catalyzed reaction. As a first step in this direction we have investigated the reduction of the nine compounds in Table 1 by classical d.c. polarography, cyclic voltammetry and preparative electrolysis.

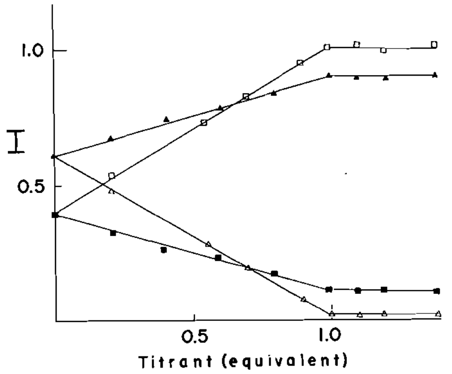


FIG. 1. Amperometric titration of NCU (**1**) (20 m*M*) in 0.2 *M* methanolic solution of $LiClO_4$. (*a*) Titrant is acetic acid: □ $I_1$, △ $(I_2 - I_1)$. (*b*) Titrant is sodium methoxyde: ■ $I_1$, ▲ $(I_2 - I_1)$. $I_1$ (at −1.0 V *vs.* s.c.e.) and $I_2$ (at −1.6 V *vs.* s.c.e.) are given in arbitrary units.

### *Polarographic Studies*

In methanolic solutions *N*-chlorourethane (NCU) (**1**), and *N*-chloroacetamide (NCA) (**2**), show two diffusion controlled reduction waves. NCU: $(E_{1/2})_1 = -0.60$ V, $(E_{1/2})_2 = -0.96$ V *vs.* a saturated calomel electrode (s.c.e.); NCA: $(E_{1/2})_1 = -0.43$ V, $(E_{1/2})_2 = -1.12$ V *vs.* s.c.e. $(E_{1/2})_1$ is p*H* independent, $(E_{1/2})_2$ is displaced cathodically only at operational p*H* values in excess of p*H* 11, but the respective currents $I_1$ and $I_2$ are p*H* dependent. The dependence is so exact that it can serve as the basis of an amperometric titration analysis illustrated in Fig. 1 for NCU (**1**).

Indeed, the waves correspond to highly irreversible two electron reduction steps involving the neutral molecule (acid) and the anion (base) respectively:

$$[1]\quad SH^+ + ZCONHCl + 2e^- \rightarrow ZCONH_2 + Cl^- + S$$

and

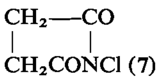
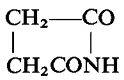
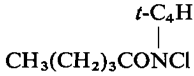
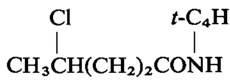
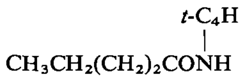
$$[2]\quad 2SH^+ + ZCO\overset{-}{N}Cl + 2e^- \rightarrow ZCONH_2 + Cl^- + 2S$$

where $SH^+$ is a proton donor (*e.g.* ZCONHCl or $CH_3OH$). The overall reactions are in perfect accord with the results of mass electrolysis (100 ± 2% coulombic efficiency) and chemical

---

[1] Taken in part from the M.Sc. thesis of J. Caza, Université de Sherbrooke, 1973.

TABLE 1. Reduction of *N*-haloamides at a mercury electrode in acetonitrile (0.2 *M* $LiClO_4$)

| *N*-Haloamide | $(E_{1/2})_1$ V *vs.* s.c.e. | $(E_{1/2})_2$ V *vs.* s.c.e. | *n* | Electrolysis products | Yield (%)[a] |
|---|---|---|---|---|---|
| $CH_3CH_2OCONHCl$ (**1**) | −0.22 | −1.22 | 2 | $CH_3CH_2OCONH_2$ | 94 |
| | −0.40(Pt) | [b] | 2 | $CH_3CH_2OCONH_2$ | 94[c] |
| $CH_3CONHCl$ (**2**) | −0.35 | −1.21 | 2 | $CH_3CONH_2$ | [d] |
| $ClCH_2CONHCl$ (**3**) | −0.11 | [b] | 2 | $ClCH_2CONH_2$ | [d] |
| $Cl_2CHCONHCl$ (**4**) | −0.09 | [b] | 2 | $Cl_2CHCONH_2$ | [d] |
| $Cl_3CCONHCl$ (**5**) | +0.05 | [b] | 2 | $Cl_3CCONH_2$ | 70 |
| | | | | $Cl_2CHCONH_2$ | 19 |
| $CH_3CONHBr$ (**6**) | −0.15 | −0.82 | [b] | [e] | |
| | −0.10(Pt) | [b] | [b] | [e] | |
|  $\begin{array}{l}CH_2{-}CO\\ \vert\qquad\ \vert\\ CH_2CONCl\end{array}$ (**7**) | −0.04 | | 2 |  $\begin{array}{l}CH_2{-}CO\\ \vert\qquad\ \vert\\ CH_2CONH\end{array}$ | [d] |
|  $\begin{array}{l}\quad\ C_2H_5\\ \quad\ \vert\\ CH_3CONCl\end{array}$ (**8**) | −0.10 | | [b] | [e] | |
|  $\begin{array}{l}\qquad\quad t\text{-}C_4H_9\\ \qquad\quad \vert\\ CH_3(CH_2)_3CONCl\end{array}$ (**9**) | −0.13 | | 1 |  $\begin{array}{l}\quad Cl\qquad\quad t\text{-}C_4H_9\\ \quad\vert\qquad\qquad \vert\\ CH_3CH(CH_2)_2CONH\end{array}$ | 37 |
| | | | |  $\begin{array}{l}\qquad\qquad\quad t\text{-}C_4H_9\\ \qquad\qquad\quad \vert\\ CH_3CH_2(CH_2)_2CONH\end{array}$ | 55 |

[a] Of isolated products.
[b] Not determined.
[c] By v.p.c. The electrolysis in the presence of an equivalent of acetic acid gave a quantitative yield of urethane.
[d] The exact yield was not determined because of the high solubility of the amides in water.
[e] No preparative electrolysis was carried out.

analysis of the products (see Preparative Electrolyses).

For electroanalytical purposes it may be noted that the polarographic diffusion currents are linear functions of the concentration from $10^{-4}$ to $5 \times 10^{-3}$ *M* and vary with the square root of the mercury column height for all compounds listed in Table 1. The half wave potentials do not vary with concentration although for compounds **3** to **6** they are somewhat ill defined (±0.05 V) due to incipient polarographic maxima.

In an aprotic medium such as acetonitrile, NCU (**1**), NCA (**2**), and *N*-bromoacetamide (NBA) (**6**) show the two reduction waves due to the neutral molecule [1] and the anion [2] respectively (Table 1). Indeed the corresponding lithium salts show the second wave only; upon addition of acetic acid, the first wave appears and when two or more equivalents of acid are added, only the first wave can be seen. The polarographic reduction of NCU (**1**) and NCA (**2**) remains truly irreversible ($\alpha n$ values of the order of 0.3 and 0.4 for the first wave) and the reduction products (urethane, acetamide) are not reoxidized even at a platinum anode before the anodic decomposition of the electrolyte. The polarographic reduction of the *N*-chloro-α-chloroacetamides **3** to **5** is also irreversible ($\alpha n \sim 0.9$, $n = 2$). At potentials more cathodic than −0.8 V *vs.* s.c.e., two or more waves appear, one being most probably due to the reduction of the N—Cl bond of the anions, and the other(s) to the reduction of the C—Cl bonds; this region was not further investigated.

Since the mechanism proposed by Lessard *et al.*[2] for the chromous chloride promoted addition of *N*-haloamides to olefins implied an amide radical species, we had hoped to be able to discern two consecutive one electron transfer steps (*e.g.* [3] and [4]) constituting [1] or [2]:

$$[3]\qquad ZCONHCl + e^- \rightarrow ZCO\dot{N}H$$

$$[4]\qquad ZCO\dot{N}H + e^- + SH^+ \rightarrow ZCONH_2 + S$$

In retrospect it may not be surprising that the insertion of the second electron [4] should be faster than or as fast as the insertion of the

---

[2] H. Driguez, J. M. Paton, and J. Lessard, presented at the 55th Chemical Conference of the Chemical Institute of Canada, Quebec, June 1972.

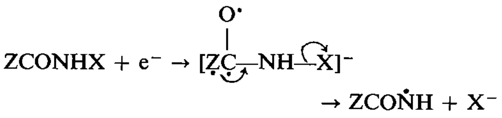
first and hence indiscernable by normal electroanalytical techniques. We also searched for chemical evidences of the formation of the amide radical [3], by coupling, trapping by hydrogen abstraction from methanol, and by addition to olefins, in preparative electrolyses at a mercury and a platinum cathode but without any success.[3] However addition products have been isolated when preparative electrolyses of NCU (**1**) were carried out at a graphite electrode in the presence of an olefin under special conditions.

Although standard electrode potentials could not be established (anodic region inaccessible), the $E_{1/2}$ values show useful trends with the chemical structures of the depolarizers (Table 1). Since we can assume that the same functional group ($—\overset{\overset{\text{O}}{\|}}{\text{C}}—\text{NH}—\text{X}$) is involved, we expect the $E_{1/2}$ values to reflect the activation energy of the first electron transfer step and also the stability of the intermediate species (7).

The two possible mechanisms for the addition of the first electron are: (*1*) addition to the N—X bond whose fission leads to the amide radical and the halide anion [5];

$$[5] \quad \text{ZCONHX} + e^- \rightarrow [\text{ZCONH} \cdots \text{X}]^{\dot{-}} \rightarrow \text{ZCO}\dot{\text{N}}\text{H} + \text{X}^-$$

(*2*) addition to the π system with the subsequent cleavage of the N–X bond (which might be concerted with the electron transfer) leading to the amide radical and the halide anion [6].[4]

[6] 

$$\text{ZCONHX} + e^- \rightarrow [\text{Z}\overset{\overset{\text{O}^\bullet}{|}}{\text{C}}\text{—NH—X}]^- \rightarrow \text{ZCO}\dot{\text{N}}\text{H} + \text{X}^-$$

For both mechanisms, one would expect that an electron withdrawing group Z should facilitate electron acceptance and render the reduction potential more anodic, but probably more so for the second mechanism. For the reduction of the *N*-chlorocarboxamides, $E_{1/2}$ becomes more anodic in the sequence **2** ($Z = CH_3$) < **3** ($Z = CH_2Cl$) < **4** ($Z = CHCl_2$) < **5** ($Z = CCl_3$), the effect being the largest for the introduction of the first chlorine. The reduction potential of NCU (**1**, $Z = OC_2H_5$) is more anodic than that of NCA (**2**, $Z = CH_3$) but more cathodic than that of *N*-chloro-α-chloroacetamide (**3**, $Z = CH_2Cl$). Although an ethoxy group should have a stronger inductive effect than a chloromethyl group, this effect should be partly compensated in the former by its ability to share its electrons with the carbonyl group of the amide. The more anodic reduction potential of *N*-chlorosuccinimide (**7**) as compared to that of *N*-chloroacetamide (**2**) can be accounted for also by either mechanism. *N*-chloro-*N*-ethylacetamide (**8**) and *N*-chloro-*N*-tertiobutylpentanamide (**9**) are more easily reduced than *N*-chloroacetamide (**2**) in agreement with the stabilizing influence of an alkyl group, as compared to an hydrogen atom, in the intermediate amide radical. Finally NBA (**6**) is more readily reduced than NCA (**2**) as expected on the basis of bond strength, polarizabilities and ease of reduction of organic (alkyl, aryl, vinyl) halides (10).

### *Preparative Electrolyses*

In methanol, using $LiClO_4$ electrolyte, the reduction of NCU (**1**) at a mercury electrode in

---

[3] The experimental results for the reduction at a mercury electrode do not allow us to distinguish between the direct reduction of the amide radical [4] and the reduction of an intermediate species resulting from the trapping of the amide radical by mercury. Mann *et al.* (5) suggested an analogous interaction of the organo radical with mercury in the reduction of a cyclopropyl bromide.

Two reduction waves have been observed for the alkylmercuric halides (6). In order to eliminate the possibility of the two reduction waves of NCU (**1**), NCA (**2**), and NBA (**6**) being due to the rapid formation of organomercuric halides upon contact with mercury, the reaction of NCU (**1**) and NBA (**6**) with mercury was investigated. The original polarographic waves disappeared slowly, a new wave appeared, and a grey precipitate, consisting primarily of colloïdal mercury and calomel, was formed. These reactions could be prevented by imposing a slightly cathodic potential on the mercury metal and were not investigated extensively (see Experimental).

[4] For the electroreduction of the vinyl halides, Miller and Riekena (8) have suggested that the first electron may add to the π system to give an anion radical which loses a halide anion to form the vinyl radical. For the reductive hydrogenolysis of *p*-carbomethoxy- and *p*-cyano-substituted benzyl methyl ether, benzyl acetate and benzylidyne trifluoride in protic medium, electron transfer to the substituent followed by the cleavage of the C—O and C—F bonds has been proposed as the first step (9).

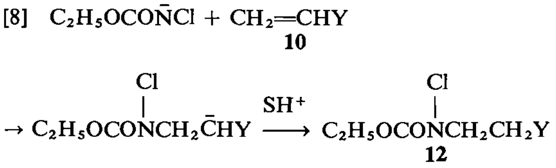
the presence of an equimolar amount of acetic acid (reduction of the neutral molecule)[5] yielded 92% (isolated) urethane. The reduction carried out in the presence of an equimolar quantity of sodium methoxyde (reduction of the anion)[5] gave a quantitative yield (by v.p.c.) of urethane. In either reduction, no *N,N′*-dicarboethoxyhydrazine (coupling of two urethane radicals) could be detected by vapor phase chromatography (v.p.c.). Also attempts to detect formaldehyde prove inconclusive.[6]

In acetonitrile ($LiClO_4$ electrolyte), the reduction of NCU (**1**) and the *N*-chloroacetamides **2** to **5** at the mercury electrode gave the corresponding amides in the yields indicated in Table 1. No traces of dimerization products (coupling of amide radicals) could be detected. The results were identical for the reduction of NCU (**1**) at a platinum electrode.

Electroreduction of NCU (**1**) in the presence of electron-poor olefins such as acrylonitrile (**10**, Y = CN) and methyl acrylate (**10**, Y = $COOCH_3$) in a methanol–chloroform (2:3) mixture readily led to the addition product $C_2H_5OCONHCH_2CH_2Y$ (**11**). The mechanism does not involve radicals but involves the addition of anions. The product may be formed directly from the urethane anion, the path followed being similar to that proposed by Baizer and Chruma (11) in their study of the reduction of organic *gem*-halides in the presence of electrophilic double bonds:

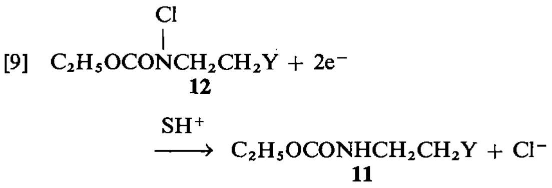
$$[7]\quad \mathrm{C_2H_5OCO\bar{N}H + CH_2{=}CHY}\ \underset{\mathbf{10}}{} \rightarrow \mathrm{C_2H_5OCONHCH_2\bar{C}HY} \xrightarrow{\mathrm{SH^+}} \underset{\mathbf{11}}{\mathrm{C_2H_5OCONHCH_2CH_2Y}}$$

where $SH^+$ is a proton donor, predominantly $C_2H_5OCONHCl$ (**1**). A ready source of protons will favor the formation of urethane (reaction 1, Z = $OC_2H_5$) while extremely low concentrations of $SH^+$ would favor polymerization reactions (11). Alternatively, the product may be formed indirectly from the NCU anion:



$$[8]\quad \underset{}{\mathrm{C_2H_5OCO\bar{N}Cl}} + \underset{\mathbf{10}}{\mathrm{CH_2{=}CHY}} \rightarrow \mathrm{C_2H_5OCO\overset{Cl}{\overset{|}{N}}CH_2\bar{C}HY} \xrightarrow{\mathrm{SH^+}} \underset{\mathbf{12}}{\mathrm{C_2H_5OCO\overset{Cl}{\overset{|}{N}}CH_2CH_2Y}}$$

followed by:



$$[9]\quad \underset{\mathbf{12}}{\mathrm{C_2H_5OCO\overset{Cl}{\overset{|}{N}}CH_2CH_2Y}} + 2e^- \xrightarrow{\mathrm{SH^+}} \underset{\mathbf{11}}{\mathrm{C_2H_5OCONHCH_2CH_2Y}} + \mathrm{Cl^-}$$

It was shown that the homogeneous reaction 8 followed by bisulfite reduction yielded **11** (*e.g.* 46% yield for Y = CN). As has been demonstrated above, the *N*-chloro-*N*-alkyl carboxamides are more readily reduced than the ZCONHCl species itself so that [9] competes favorably with [1]. In mass electrolysis **12** is thus readily reduced and **11** constitutes the major product (50% yield for Y = CN, 61% yield for Y = $COOCH_3$).[7] No trace of α-chlorinated products ($\mathrm{C_2H_5OCONHCH_2\overset{Cl}{\overset{|}{C}}HY}$) expected from a radical chain mechanism could be detected.

Reduction of NCU (**1**) at a mercury cathode in acetonitrile in the presence of norbornene (10 fold excess) gave urethane only according to v.p.c. analysis. No traces of addition products could be detected. Thus, if a radical is indeed formed upon addition of the first electron [3], it would seem that in the competition between the insertion of a second electron and the chemical reaction, the former usually wins out. This is in direct contrast to the chromous chloride catalysed addition of *N*-chlorourethane to olefins where each Cr(II) ion can contribute but one electron. There, the competition depends on the chance encounter with a second chromous ion or the olefin. In that case addition was favored by maintaining the concentration of the discrete electron source, the Cr(II)

---

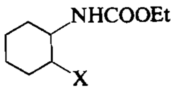
[5] NCU (**1**) is a weaker acid than acetic acid ($\Delta pK_a = 3.3$ in methanol–water 1:1) but much stronger than methanol.

[6] Formaldehyde was formed in the chromous chloride reduction of NCU (**1**) in methanol as the result of hydrogen abstraction from methanol by the urethane radical (see footnote 2).

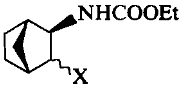
[7] No attempt was made to identify the nature of the remaining products.

species, as low as practical. At the electrode however, a virtually unlimited supply of electrons is available and it becomes necessary to enhance the chances of chemical reaction.

In order to increase the concentration of olefin near the electrode we employed a cathode consisting of a graphite paste constituted by mixing NCU (**1**) with a five fold excess of cyclohexene or norbornene. After electrolysis for nine hours at room temperature the *cis* and *trans* addition products were obtained, analyzed, and isolated. With cyclohexene, a 18% yield of 1,2-adducts **13** and **14** (*cis–trans* 0.5:1) was obtained, and with norbornene the yield was 14% of **16** and **17** (*cis–trans* 1:1). Urethane still constituted the major product. In a control experiment in which the graphite paste (NCU (**1**) and cyclohexene) was kept at room temperature for ten hours, there was an 8% loss of active chlorine (iodometric titration) and formation of *ca.* 0.9% (by v.p.c.) of 1,2-adducts **13** and **14** (*cis–trans* 0.5:1).

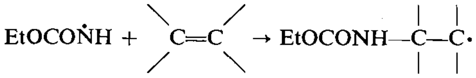


**13** X = Cl (*cis*)
**14** X = Cl (*trans*)
**15** X = H

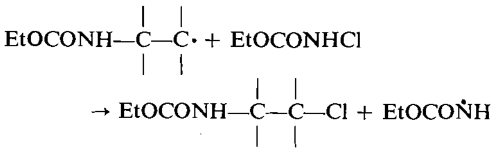


**16** X = Cl (*exo*)
**17** X = Cl (*endo*)
**18** X = H

Thus it seems probable that, in the above electrolyses, most of the addition products were formed via the electrochemically generated urethane radical [3] by a chain mechanism:

[10] 

$$\mathrm{EtOCO\dot{N}H} + \mathrm{C{=}C} \rightarrow \mathrm{EtOCONH{-}C{-}C\cdot}$$

[11] 

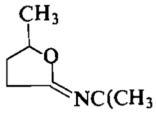
$$\mathrm{EtOCONH{-}C{-}C\cdot} + \mathrm{EtOCONHCl} \rightarrow \mathrm{EtOCONH{-}C{-}C{-}Cl} + \mathrm{EtOCO\dot{N}H}$$

Chain termination by a second electron transfer step to the radical according to [4] is in fair accord with the number of coulombs passed and p*H* changes. No traces of the reduced products, *N*-cyclohexylurethane (**15**) or *N*-(2-*exo*-norbornyl)urethane (**18**), could be detected. Compound **18** is the major product (54%) in the chromous ion reduction of NCU in the presence of norbornene (1).

The addition products **13** to **18** were shown to be much more difficult to reduce than NCU and thus, once formed, unlikely to disappear during electrolysis. We therefore conclude that the reduction of the intermediate β-amidoalkyl radical must be slower than its reaction with NCU [11].

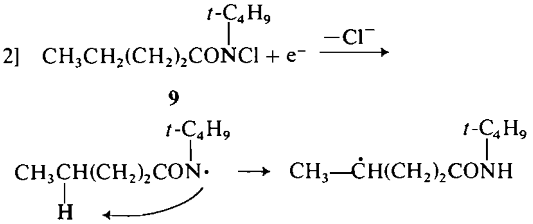
In order to confirm the intervention of an amide radical in the electrolytic reduction of the *N*-chloro-*N*-alkyl carboxamides we employed another approach since the addition of *N*-alkylamido radicals to olefins is more difficult than the addition of the corresponding *N*-hydroamido radicals (3, 4). Neale *et al.* (12) have shown that aliphatic ($C_4$ to $C_6$) *N*-chloro-*N*-alkyl carboxamides can be rearranged photolytically to the 4-chloro derivative, the preferred *N*-substituent being the *t*-butyl group. For instance, photolysis of *N*-chloro-*N*-*t*-butyl pentanamide (**9**) in benzene gave the 4-chloro derivative **19** and *N*-*t*-butyl pentanamide (**20**) in a 43% and 42% yield respectively (12). The radical chain reaction involved include a selective intramolecular hydrogen abstraction at $C_4$ by the amide radical through a six atom transition state.

Electrolysis of *N*-chloro-*N*-*t*-butyl pentanamide (**9**) at the mercury cathode yielded 37% of the 4-chloro derivative **19** and 55% of the carboxamide **20** for a total product yield of 92% (the proportion of **19** and **20** was calculated from the n.m.r. spectrum of the crude product. The chemical proof of the presence of **19** was obtained by the synthesis of the iminolactone **21**).

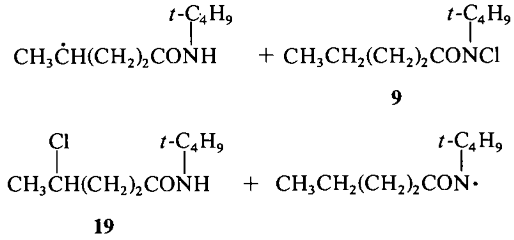


**21**

Here the product yield is competitive with the photolysis results. The coulombic efficiency was close to 200%, clearly indicating a radical-chain mechanism:

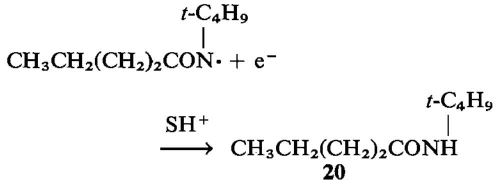
[12] 

$$\underset{\mathbf{9}}{\mathrm{CH_3CH_2(CH_2)_2CO\overset{\textit{t}\text{-}C_4H_9}{N}Cl}} + e^- \xrightarrow{-\mathrm{Cl}^-} \mathrm{CH_3\underset{H}{C}H(CH_2)_2CO\overset{\textit{t}\text{-}C_4H_9}{N}\cdot} \longrightarrow \mathrm{CH_3{-}\dot{C}H(CH_2)_2CO\overset{\textit{t}\text{-}C_4H_9}{N}H}$$

[13]


$$\mathrm{CH_3\dot{C}H(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}H} + \underset{\mathbf{9}}{\mathrm{CH_3CH_2(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}Cl}} \longrightarrow \underset{\mathbf{19}}{\mathrm{CH_3\overset{\overset{\displaystyle Cl}{|}}{C}H(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}H}} + \mathrm{CH_3CH_2(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}\cdot}$$

The main chain termination step most likely involves the reaction 14 giving rise to **20**:

[14]


$$\mathrm{CH_3CH_2(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}\cdot} + e^- \xrightarrow{SH^+} \underset{\mathbf{20}}{\mathrm{CH_3CH_2(CH_2)_2CO\overset{\overset{\displaystyle t\text{-}C_4H_9}{|}}{N}H}}$$

Under conditions identical to those of the electrolysis but without applying any potential, the *N*-chloroamide **9** reacted with mercury (31% loss of active chlorine) with the formation of a black precipitate. No 4-chloro-*N*-*t*-butyl-pentanamide (**19**) could be detected, the sole organic product formed being the pentanamide **20**. Therefore the formation of the 4-chloro derivative **19** during the electrolysis most probably involves the electrochemically generated amide radical [12].

## Conclusions

The electroreduction of *N*-halocarboxamides and *N*-chlorourethane (**1**) in aprotic and protic media proceeds at the mercury electrode at $E_{1/2}$ potentials depending on the chemical nature of the depolarizer, the p*H* and to a lesser degree the nature of the solvent. The reduction involves two consecutive one electron steps. The very irreversible first electron transfer and formation of a radical species is followed by a considerably faster uptake of the second electron to form the anion. We believe that the intermediate radical in the reduction of NCU (**1**) has been trapped under special conditions by intermolecular addition to olefins. In the case of *N*-chloro-*N*-*t*-butyl pentamide (**9**) the radical has been captured by intramolecular hydrogen abstraction to a degree offering possible applications in synthesis. The addition of NCU (**1**) to acrylonitrile and methylacrylate has been shown to proceed readily and to involve the addition of anions.

## Experimental

### Solvents and Electrolyte

Acetonitrile (Fischer ACS reagent) was purified by distillation from phosphorous pentoxide. Chloroform (anhydrous reagent, Fischer) was used without further purification and absolute methanol was obtained by standard procedure. Lithium perchlorate (anhydrous reagent, Alfa Inorganics Co.) was used after drying in a vacuum oven for 24 h at 100 °C.

### Electrochemical Instrumentation

A three electrode potentiostat (Tacussel type ASA 100) with an automatic drop dislodger (Tacussel type MPO3) or a rotating platinum electrode (Tacussel type Controvit) was used to record respectively the polarograms and voltammograms. Potentials were measured with respect to an aqueous saturated calomel electrode with a KCl saturated agar salt bridge separated from the electrolysis vessel by a compartment containing supporting electrolyte between two fritted glass discs in order to prevent water contamination.

A glass cell of concentric construction containing the anode in a central compartment separated by a fritted glass disc from the exterior catholyte compartment (50 or 200 ml volume) was employed for mass electrolysis. A three electrode system controlled by a Tacussel type ASA 100 potentiostat was employed for all but the electrolysis involving a graphite paste electrode. In the latter case the high resistance of the porcelaine cup (see below) rendered potentiostatic control impossible unless the reference electrode was buried in the carbon paste, but the conditions employed (both electrolysis at fixed current and constant applied potential) correspond to about 1/5 of the limiting current and entail little danger of provoking alternate reactions. For coulometric determination the progress of the electrolysis was followed by recording polarograms after a fixed number of coulombs had passed and by iodometric titration of the remaining halogen derivatives. The charge passed was obtained by graphically integrating the current time curves and by using an electrochemical coulometer.

All voltammetric analyses as well as mass electrolyses were carried out in a nitrogen atmosphere. For the polarographic reduction of *N*-bromoacetamide (**6**), Nujol was added at the bottom of the cell to isolate the solution from mercury and the cell was cooled in an ice bath. In mass electrolyses, a slight negative potential was applied at the mercury electrode before adding the *N*-haloamide in order to prevent the formation of a precipitate (see reaction of *N*-haloamides with mercury).

### Analysis of Products and Starting Materials

Melting points were determined on a Büchi apparatus and are uncorrected. The i.r. spectra were determined on a Perkin-Elmer 257 spectrometer. The n.m.r. spectra were recorded on a Varian A-60 instrument and chemical shifts are reported in δ. The mass spectra were taken on a Hitachi RMU-6E spectrometer. The v.p.c. analyses were performed on a Hewlett Packard chromatograph model 5750 equipped with both thermal conductivity and flame-ionization detectors. A 6 ft × 0.25 in. OS-138 on Chromosorb W column was used. Merck silica gel $GF_{254}$ was used for thin and preparative layer chromatography. Organic phases from extractions were dried over anhydrous sodium sulfate.

*N-Haloamides*

*N*-Chlorourethane (**1**) (88% active chlorine), *N*-chloro-2-chloroacetamide (**3**) and *N*-chloro-2,2-dichloroacetamide (**4**) (100% active chlorine) were prepared from the corresponding amides by the sodium hypohalite method (13). *N*-Chloroacetamide (**2**) was prepared according to the method described by Orton and Bradfield (14), m.p. 109–110 °C (100% active chlorine). *N*-Chloro-2,2,2-trichloroacetamide (**5**) was prepared according to the method of Park *et al.* (15), m.p. 124–125 °C (100% active chlorine). *N*-Chloro-*N*-ethylacetamide (**8**) was prepared by treatment of an aqueous solution of the corresponding amide containing sodium bicarbonate with chlorine followed by extraction with methylene chloride and distillation under reduced pressure; b.p. 46–47 °C (15 Torr) (96% active chlorine, 75% yield). *N*-Chloro-*N*-tertiobutylpentanamide (**9**) was prepared by the method described by Neale *et al.* (12) in a 65% yield (85% active chlorine). The *N*-bromoacetamide (**6**) and *N*-chlorosuccinimide (**7**) were obtained commercially (Aldrich Chemical Co.) and were recrystallized from methylene chloride (> 99% active chlorine).

The lithium salts of NCU (**1**) and NBA (**6**) were obtained as a foam by treating the *N*-haloamide with an equimolar amount of lithium methoxyde in anhydrous methanol and evaporating to dryness under vacuum.

*Reaction of N-Haloamides with Mercury*

*N-Chlorourethane (1)*

A solution of 626 mg (99% active chlorine, 5.07 mmol) of NCU (**1**) in 10 ml of a 0.2 *M* $LiClO_4$ solution in acetonitrile was stirred at room temperature with 11 g of mercury under a nitrogen atmosphere. A grey precipitate began to appear after a few minutes. The reaction was followed by polarography. A new wave appeared at +0.10 V *vs.* s.c.e., the waves due to NCU and its anion disappearing gradually. The current of the new wave reached a maximum after 5.5 h corresponding to 48% of $I_1 + I_2$ of the starting solution and then decreased slightly. After 20 h the reaction mixture was filtered and the precipitate washed with acetonitrile then methylene chloride. The resulting solution was concentrated under reduced pressure (~10 ml) and water (40 ml) was added. There was no NCU left according to iodometric assay. Continuous extraction with methylene chloride afforded 253 mg of urethane (56% yield). The grey precipitate (3.9 g) was treated with dilute nitric acid and the resulting solution continuously extracted with methylene chloride to yield an additional 82 mg of urethane (total yield of 74%).

The reaction was repeated and the precipitate was isolated after 3 h, dried, and analyzed for mercury and chloride ion: Hg, 92.6 ± 1.1%; $Cl^-$, 4.1 ± 0.4%; the remaining 3% was probably organic in nature.

The reaction was carried out in $CD_3CN$ and followed by n.m.r., each aliquot being carefully freed from the solid suspension. After a few hours, the spectrum showed only unresolved broad absorptions for possibly NH protons and protons of an ethoxycarbonyl group. After 24 h, the spectrum was well resolved and identical to that of urethane.

*N-Bromoacetamide (6)*

The reaction was carried out on 0.98 mmol of NBA in the polarographic cell. A white precipitate was formed immediately upon the addition of mercury and became grey after a few minutes. The wave at *ca.* −0.1 V *vs.* s.c.e. disappeared while a new wave at −0.29 V was appearing. After 4 h the polarogram showed only this new wave. No attempt was made to isolate and characterize the products.

*N-Chloro-N-tertiobutylpentanamide (9)*

A solution of 1.13 g (85% active chlorine, 4.95 mmol) of *N*-chloro-*N*-tertiobutylpentanamide (**9**) in 10 ml of a 0.2 *M* $LiClO_4$ solution in acetonitrile was stirred at room temperature with 4 g mercury under a nitrogen atmosphere. A black precipitate began to appear almost as soon as mercury was added. After 24 h, the reaction mixture was filtered, worked up in the usual way, analyzed for active chlorine (3.40 mmol, 69% of unreacted **9**), then treated with a saturated solution of sodium bisulfite until the reduction of active chlorine was completed. Extraction with methylene chloride gave 0.825 g of *N*-tertiobutylpentanamide (**20**), m.p. 44–47 °C (89% by taking into account the 15% present in the starting material). The presence of the 4-chloro-derivative **19** could not be detected in the n.m.r. spectrum. The precipitate (2.24 g) was analyzed for mercury and chloride ion: Hg, 97.2 ± 0.3%; $Cl^-$ (as $Hg_2Cl_2$), 2.6 ± 0.1% (total of 99.8 ± 0.3%). An X-ray powder diffraction analysis confirmed the presence of the crystalline $Hg_2Cl_2$ phase.

An identical solution of the *N*-chloroamide **9** kept at room temperature for 24 h but without adding mercury gave the following results: 4.75 mmol (92%) of unreacted **9**; 0.850 g of *N*-tertiobutylpentanamide (**20**), m.p. 43–47 °C (91%) after reduction with sodium bisulfite.

*Electrolyses*

Some typical electrolyses are summarized below.

*Electroreduction of N-Chlorourethane (1)*

*In Methanol*—A solution of 1.22 g (88% active chlorine, 10 mmol) of *N*-chlorourethane (**1**) and 0.6 g (10 mmol) of acetic acid in 50 ml of a 0.2 *M* methanolic solution of $LiClO_4$ was electrolyzed at a cathode potential of −0.7 V. The anode compartment (auxiliary electrode, Mg) contained 5 to 7 ml of the 0.2 *M* electrolyte solution. The electrolysis was discontinued when no more active chlorine was present (negative potassium iodide – starch paper test). The catholyte was poured into water (*ca.* 50 ml) then extracted with methylene chloride (3 × 100 ml). The organic layers were washed with water then combined and dried. The solution was concentrated to a volume of *ca.* 50 ml by distilling the solvent and then analyzed by v.p.c. (170 °C). Urethane was the main component. No traces of the dimer *N,N'*-dicarboethoxyhydrazine could be detected. Small amounts of products with lower retention times than that of urethane were present and were not investigated. Removal of the solvent in the rotatory evaporator left 0.81 g (92%) of urethane, m.p. 43–45 °C, identified further by comparison of the i.r. and n.m.r. spectra with those of an authentic sample (Aldrich Chemical Co.).

The electrolysis carried out in the presence of an equimolar (10 mmol) amount of sodium methoxyde (instead of acetic acid) and at a cathode potential of −1.2 V, the other conditions being exactly the same as above, gave urethane only according to the v.p.c. analysis (100% yield).

*In Acetonitrile*—The electrolysis was carried out on 10 mmol as described above except that acetonitrile was used as solvent and no base or acid was added. The cathode potential was $-0.3$ V (auxiliary electrode, Mg). The usual work-up gave, after complete evaporation of the solvent, 0.84 g (94%) of urethane, m.p. 44–45 °C. The dimer *N,N'*-dicarboethoxyhydrazine could not be detected by v.p.c. analysis.

The electrolysis was repeated in the presence of an excess of norbornene (100 mmol). Urethane was the only product formed according to the v.p.c. analysis. No traces of the adducts **16**, **17** or **18** could be detected.

### *Electrochemical Reduction of N-Chloro-2,2,2-trichloroacetamide (5)*

A solution of 315 mg (1.50 mmol) of *N*-chloro-2,2,2-trichloroacetamide (**5**) in 50 ml of a 0.2 *M* solution of $LiClO_4$ in acetonitrile was electrolyzed at a cathode potential of $-1.0$ V (auxiliary electrode, Mg) until the test for active chlorine was negative. The usual work-up followed by evaporation of the solvent left 155 mg of a crystalline residue. The v.p.c. analysis showed that it consisted of trichloroacetamide and dichloroacetamide in a 9:1 ratio (authentic samples were used as standards). Crystallization from methylene chloride gave practically pure trichloroacetamide, m.p. 138–140 °C. Continuous extraction with methylene chloride for several days gave an additional 16 mg of 2,2-dichloroacetamide. Thus the yield of trichloroacetamide was 70% and that of dichloroacetamide 19%. Both amides were further identified by the comparison of their i.r. spectra with those of authentic samples.

### *Electroreduction of N-Chlorourethane (1) in the Presence of Methyl Acrylate and Acrylonitrile*

*Methyl Acrylate*—The cathode compartment was filled with 50 ml of a 0.2 *M* $LiClO_4$ solution in a 2:3 mixture of absolute methanol and chloroform and 42 ml (40 g, 465 mmol) of methylacrylate were added. The anode compartment (auxiliary electrode, Pt) contained 10 to 15 ml of the electrolyte solution. A potential of $-0.3$ V was applied and 8 ml of a 2.25 *M* *N*-chlorourethane (**1**) solution (18 mmol) in methanol–chloroform 2:3 were added dropwise in order to maintain a current of 50 mA. The addition took 3 h and, after the current had reached 10 mA, 20 ml of a saturated $NaHSO_3$ solution were added to reduce the active chlorine left. The mixture was extracted with methylene chloride ($3 \times 100$ ml). The organic layers were combined and dried. The resulting solution was concentrated in the rotatory evaporator then transferred into a 50 ml volumetric flask with methylene chloride. Analysis by v.p.c. (180 °C) showed that methyl 3-carboethoxyaminopropionate (**11**, $Y = COOCH_3$) was formed in a 61% yield. An authentic sample prepared from β-alanine[8] was used as standard. Evaporation of the solvent followed by distillation of the residue under reduced pressure gave 1.51 g (48%) of adduct **11** ($Y = COOCH_3$), b.p. 134 °C (5 Torr), identified with the authentic material by comparison of the i.r. and n.m.r. spectra.

*Acrylonitrile*—The reduction was carried out exactly as described above except that methylacrylate was replaced by acrylonitrile (500 mmol). Microdistillation of the residue at 115 °C (1 Torr) afforded 0.53 g of a mixture of urethane and compound **11** (Y = CN). Separation of an aliquot by preparative v.p.c. (OS-138, 175 °C, 6 ft × 3/8 in. column) gave the pure 3-carboethoxyaminopropionitrile (**11**, Y = CN) but with low recovery due to decomposition on the column; $\upsilon_{max}$ ($CHCl_3$) 3420 (>NH), 2240 (—C≡N), 1720 (amide I), 1515 (amide II), 1250 and 1200 $cm^{-1}$ (—CO—O—Et); δ ($CHCl_3$), 1.25 (t, $J = 7$ Hz, $CH_3$—$CH_2$—O—), 2.62 (t, $J = 7$ Hz, —$CH_2$—$CH_2$—CN), 3.50 (q, $J = 7$ Hz, —NH—$CH_2$—$CH_2$—), 4.20 (q, $J = 7$ Hz, $CH_3$—$CH_2$—O—), and 5.22 (m, —NH—); *m/e* 142 ($M^+$).

The reaction was repeated and the yield of **11** (Y = CN) was determined by v.p.c. using the pure sample obtained above as standard: 50%.

### *Addition of the Lithium salt of N-Chlorourethane (1) to Acrylonitrile*

The solution of 18 mmol of *N*-chlorourethane in 150 ml of a 2:3 mixture of absolute methanol and chloroform was treated with an equimolar amount of lithium methoxyde (prepared from lithium metal and absolute methanol). Excess acrylonitrile (33 ml) was added and the mixture was kept at room temperature overnight under a nitrogen atmosphere. Sodium bisulfite (20 ml of a saturated aqueous solution) was added to reduce the active chlorine and the mixture was extracted with methylene chloride ($3 \times 100$ ml). The organic layers were combined and dried, and the solvent was removed at the rotatory evaporator. Analysis by v.p.c. (175 °C) showed that 3-carboethyoxyaminopropionitrile (**11**, Y = CN) was formed in a 46% yield using the authentic sample obtained above as standard.

### *Electroreduction of N-Chlorourethane (1) at Graphite Cathode in the Presence of Olefins*

*In the Presence of Cyclohexene*—In a cylindrical ($20 \times 175$ mm) porous porcelain crucible were placed 6 g of graphite powder, 3.50 g (88% active chlorine, 25 mmol) of *N*-chlorourethane (**1**) and 10 ml (8.1 g, 99 mmol) of cyclohexene. The mixture was stirred with a glass rod until an homogeneous paste was obtained. The electrical contact was ensured by a graphite rod immersed in the paste. A cylindrical platinum anode surrounded the cathode compartment and the anolyte consisted of 50 ml of a 0.2 *M* solution of $LiClO_4$ in acetonitrile. A potential of $-10$ V was applied between the two electrodes and the electrolysis was discontinued when the active chlorine test (potassium iodide - starch paper) was negative; 2789 coulombs ($29 \times 10^{-3}$ F) were passed in 9 h. The anolyte was extracted with methylene chloride in the usual manner after the addition of water (*ca.* 20 ml). The two solutions were combined, concentrated, then transferred into a 50 ml volumetric flask. The v.p.c. analysis gave the following results: urethane, 66%; ethyl *cis*-*N*-(2-chlorocyclohexyl)carbamate (**13**), 6%; and ethyl *trans*-*N*-(2-chlorocyclohexyl)carbamate (**14**), 12%. Authentic samples of **13** and **14** (1) were used as standards. No trace of *N*-cyclohexylurethane (**15**) could be detected. The isolation of compounds **13** and **14** for complete identification is described below.

The solution above was further concentrated and ether was added. A crystalline product was collected

---

[8] H. Driguez, Ph.D. Thesis, Université de Sherbrooke, 1971.

(580 mg, m.p. 134–135 °C) and was identified as *trans-N*-(2-chlorocyclohexyl)acetamide by comparison of the i.r. and n.m.r. spectra with those of an authentic sample.[8] The formation of this product can be explained by the diffusion of cyclohexene from the catholyte to the anolyte since Faita *et al.* (16) have shown that the oxidation of chloride ions in the presence of cyclohexene in acetonitrile gave *trans-N*-(2-chlorocyclohexyl)acetamide, the chloride ions being provided in the present case by the reduction of *N*-chlorourethane (**1**).

Separation of the mother liquors by preparative layer chromatography on silica gel afforded 1.22 g of urethane (48% taking into account the presence of 12% in the starting material), 0.27 g (5%) of the *cis* adduct **13** m.p. 53–56 °C, and 0.59 g (12%) of the *trans* adduct **14** m.p. 90–92 °C. Both adducts were fully identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples (1).

In a control experiment the graphite paste was kept at room temperature for 10 h under a nitrogen atmosphere without applying any potential. After work up as above, the solution was analyzed for active chlorine: 4.6 mmol, 92% of unreacted NCU (**1**). The active chlorine was reduced with a saturated sodium bisulfite solution. The organic phase was washed with water then dried. The v.p.c. analysis gave the following results: urethane, 96%; *cis* 1,2-adduct **13**, ~0.3%; *trans* 1,2-adduct **14**, ~0.6%.

*In the Presence of Norbornene*—The reaction was carried out as described above for cyclohexene with 9.0 g (95 mmol of norbornene and 3.20 g (88% active chlorine, 22.8 mmol) of *N*-chlorourethane (**1**). No active chlorine was present after 962 coulombs ($9.96 \times 10^{-3}$ F) were passed. The methylene chloride washings of the catholyte and the methylene chloride phases from the extraction of the anolyte were combined and the solvent removed in the rotatory evaporator. The residue was separated by preparative layer chromatography on silica gel to yield 0.80 g (35%, taking into account the presence of 12% in the starting material) of urethane, 0.36 g (7%) of ethyl *N*-[2-*exo*-(3-*exo*-chloronorbornyl)]-carbamate (**16**), m.p. 45–58 °C, and 0.33 g (7%) of ethyl *N*-[2-*exo*-(3-*endo*-chloronorbornyl)]carbamate (**17**), m.p. 85–88 °C. Both 1,2-adducts **16** and **17** were fully identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples (1). The v.p.c. analysis of the other fractions showed no trace of *N*-*exo*-norbornylurethane (**18**), and they were not examined further.

### *Electroreduction of N-Chloro-N-tertiobutylpentamide (9)*

A solution of 4.18 g (85% active chlorine, 18.5 mmol) of *N*-chloro-*N*-tertiobutylpentanamide (**9**) in 25 ml of 0.2 *M* $LiClO_4$ in acetonitrile was electrolyzed at a cathode potential of −0.3 V. The anode compartment (Pt auxiliary electrode) contained 10 ml of the 0.2 *M* electrolyte solution. The electrolysis was discontinued when no more active chlorine was present (23 h at a current of *ca.* 10 mA). The usual working-up (addition of water, methylene chloride extractions, etc.,) gave 2.93 g of crude product. The n.m.r. spectrum was compared with that of the crude product obtained from the photolysis of the same *N*-chlorocarboxamide **9** carried out as described by Neale *et al.* (12). The weight ratio of *N*-tertiobutylpentanamide (**20**) to *N*-tertiobutyl-4-chloropentanamide (**19**) was calculated to be approximately 1:2 from the relative integration of the protons of the terminal methyl group which appears at 0.9 δ (ill-defined triplet) in the carboxamide **20** and at 1.51 δ (d, $J =$ 6 Hz) in the 4-chloroderivative **19**. Thus assuming that the carboxamide **20** and the 4-chloro derivative **19** were the sole components of the crude product (in fact some impurities were present in small amount, <5% according to the n.m.r. spectra), the yield of the 4-chlorocarboxamide **19** is 37% and that of the carboxamide **20**, 55%.

A chemical proof of the presence of the 4-chlorocarboxamide **19** in the crude product was obtained in the following manner. An aliquot of 1.46 g of the crude product from the electroreduction was treated with an excess of silver perchlorate (10 mmol) in 50 ml of 50% aqueous acetonitrile at 60 °C for 1 h. The mixture was poured onto crushed ice, treated with 5% NaOH, then extracted with ether (3 × 50 ml). The ether layers were combined and dried. Removal of the ether by distillation was followed by microdistillation of the residue at 69 °C (10 Torr) to give 0.26 g of the iminolactone **21**. The i.r. and n.m.r. spectra were identical to those of the sample obtained by the same procedure from the photolysis crude product. The hydrochloride had m.p. 120–121 °C (lit. (12), m.p. 123 °C).

Support for this work by the Ministère de l'Education, Québec, and the National Research Council of Canada is gratefully acknowledged.

1. J. LESSARD and J. M. PATON. Tetrahedron Lett. 4883 (1970).
2. J. LESSARD, H. DRIGUEZ, and J. P. VERMES. Tetrahedron Lett. 4887 (1970).
3. D. TOUCHARD and J. LESSARD. Tetrahedron Lett. 4425 (1971).
4. D. TOUCHARD and J. LESSARD. Tetrahedron Lett. 3827 (1973).
5. C. K. MANN, J. L. WEBB, and H. M. WALBORSKY. Tetrahedron Lett. 2249 (1966).
6. N. S. HUSH and K. B. OLDAM. J. Electroanal. Chem. **6**, 34 (1962).
7. P. ZUMAN. Substituent effects in organic polarography. Plenum Press, New York 1967. p. 23 ff.
8. L. L. MILLER and E. RIEKENA. J. Org. Chem. **34**, 3359 (1969).
9. J. P. COLEMAN, H. G. GILDE, J. H. P. UTLEY, and B. C. L. WEEDON. Chem. Commun. 738 (1970).
10. M. R. RIFI. *In* Organic electrochemistry, *edited by* M. M. Baizer. Marcel Dekker, Inc., New York, N.Y. 1972. p. 279.
11. M. M. BAIZER and J. L. CHRUMA. J. Org. Chem. **37**, 1951 (1972).
12. R. S. NEALE, N. L. MARCUS, and R. SCHEPERS. J. Am. Chem. Soc. **88**, 3056 (1966).
13. C. BACHAND, H. DRIGUEZ, J. M. PATON, D. TOUCHARD, and J. LESSARD. J. Org. Chem. **39**, 3136 (1974).
14. K. J. P. ORTON and A. E. BRADFIELD. J. Chem. Soc. 986 (1927).
15. J. D. PARK, H. J. GERJOVICH, W. R. LYCAN, and J. R. LACHER. J. Am. Chem. Soc. **74**, 2189 (1952).
16. G. FAITA, M. FLEISCHMANN, and D. PLETCHER. J. Electroanal. Chem. **25**, 455 (1970).